

Chemical evolution and early Earth's and Mars' environmental conditions¹

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Abstract

Life originated more than 3.5 billion years ago either on Earth or on our neighbour planet Mars from where it reached Earth by lithopanspermia. Life's origin was preceded by an abiotic chemical evolution. As there is practically no geological record of this early chemistry, laboratory simulations are of special importance. However, simulation experiments are only relevant if they take the primordial physical and geochemical conditions into account. In this review, first the environmental conditions on the early Earth and Mars, as far as they are currently known, are described. Then the general features of a hypothesis on the heterotrophic origin of life are discussed. This hypothesis assumes that a rudimentary metabolism had to evolve before the first functional polymers could form. Finally the behaviour of amino acids at primordial hot volcanic coasts is discussed and serves as a case study for the simulation of environmental conditions.

Key words: Abiotic syntheses, amino acids, chemical evolution, Early Archean, Hadean, heterotrophic origin of life, metabolism-first hypotheses, Noachian, prebiotic chemistry, primordial environments, protocells, simulation experiments, volcanic islands.

Zusammenfassung

Das Leben entstand vor mehr als 3,5 Milliarden Jahren entweder auf der Erde oder auf unserem Nachbarplaneten Mars, von wo es die Erde durch Lithopanspermie erreichte. Dem Ursprung des Lebens ging eine abiotische chemische Evolution voraus. Da es praktisch keine geologischen Zeugnisse dieser frühen Chemie gibt, kommt Laborsimulationen eine besondere Bedeutung zu. Simulationsexperimente sind jedoch nur dann zweckdienlich, wenn sie die physikalischen und geochemischen Urbedingungen berücksichtigen. In dieser Übersichtsarbeit werden zunächst die Umweltbedingungen auf der frühen Erde und dem frühen Mars, soweit sie gegenwärtig bekannt sind, beschrieben. Dann werden die Grundzüge einer Hypothese über den heterotrophen Ursprung des Lebens behandelt. Diese Hypothese geht davon aus, dass sich ein rudimentärer Stoffwechsel entwickeln musste, bevor die ersten funktionsfähigen Polymere entstehen konnten. Abschließend wird das Verhalten von Aminosäuren an heißen vulkanischen Urküsten diskutiert und dient als Fallstudie zur Simulation von Umweltbedingungen.

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1. Introduction

Currently, there are two main scientific hypotheses about the origin of life on Earth. One is lithopanspermia, the idea that organisms reached the young Earth in rocks that had been ejected from another inhabited planet by asteroid impacts. Several obstacles would have had to be overcome: for example the impact (temperature, acceleration), conditions in space (radiation, vacuum), atmospheric entry, and finding suitable survival and growth conditions on Earth (CLARK 2001). Nevertheless lithopanspermia is

far from being “science fiction”. It has been concluded from an elaborate study which combined theoretical and experimental results that the natural transfer of viable microbes from Mars to Earth was and is highly probable, provided that microbes exist(ed) on Mars (MILEIKOWSKY et al. 2000). Some microorganisms such as *Bacillus subtilis* spores and dormant cells of *Deinococcus radiodurans* are sufficiently resistant against radiation, desiccation and other unfavourable environmental conditions to survive in meteoroids for a long time (HORNECK 2003). The Mars-to-Earth transfer is favoured by the comparatively low

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escape velocity of Mars (5 km/s) and the proximity of the two planets, which allows relatively short travelling times. In contrast to a transfer within our solar system, the same process between different planetary systems, i. e. the seeding of Earth from an exoplanet, appears to be at least much less probable if not impossible (MELOSH 2003; ADAMS & SPERGEL 2005; VALTONEN et al. 2009).

The other hypothesis, or rather class of hypotheses, assumes a terrestrial origin of life (DAVIS & MCKAY 1996). The basic idea is that living systems emerged from inanimate matter by chemical evolution directly on Earth. However, it is also possible that the transition from non-living to living occurred on Mars and that the Martian organisms came to Earth by lithopanspermia. This illustrates that lithopanspermia is, strictly speaking, not a hypothesis about the origin of life but about its spreading in space. Therefore the answer to the question how life initially came into existence must be sought in the framework of chemical evolution. The outcome of the chemical reactions on the early Earth and Mars was determined by the physical and geochemical conditions. Consequently, experimental and theoretical simulations must be strictly consistent with reasonable assumptions about the primordial environments. Otherwise there is a risk that implausible reactions become “prebiotically relevant” by wishful thinking.

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2. Prebiotic environmental conditions

Fig. 1 shows a time scale for chemical evolution. Shortly after the Big Bang only the three lightest chemical elements hydrogen, helium and lithium existed. A few hundred million years later the first stars were born and began to produce heavier elements. When our solar system accreted 4.6 billion years (Ga) ago from the remnants of one or more supernovae, there was already a rich abiotic chemistry in space including complex organic molecules. Currently, more than 130 molecules have been identified in the interstellar medium (ALLAMANDOLA 2008). When the Earth formed 4.57 Ga ago, it was initially covered by a hot magma “ocean” which had to cool and solidify before prebiotic chemistry could continue. 3.82 Ga old rocks from West Greenland are the oldest unequivocal evidence for the existence of a solid continental crust and liquid water (MOORBATH 2005). This was the time when the Hadean eon (4.57–3.8 Ga) ended and the Archean began. From studies on the oldest known terrestrial minerals, the Jack Hills

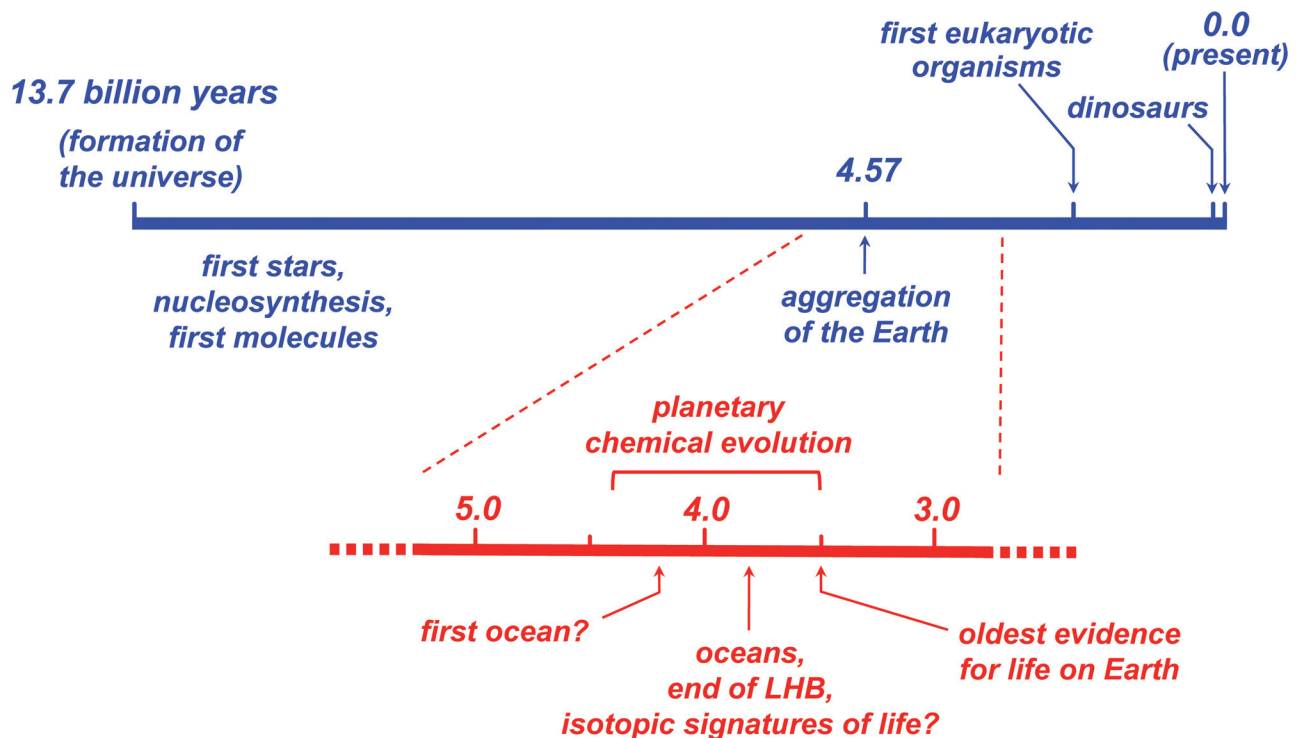


Fig. 1. Time scale for chemical evolution. Numbers are in billion years (Ga). LHB stands for Late Heavy Bombardment.

zircons ($ZrSiO_4$) from Australia, the presence of a continental crust and oceans as early as 4.3–4.4 Ga ago has been inferred (WILDE et al. 2001; MOJZSIS et al. 2001; WATSON & HARRISON 2005; HARRISON et al. 2005). However, these conclusions, in particular those relating to the existence of oceans, are not undisputed (HOSKIN 2005; NEMCHIN et al. 2006). One can take the provisional view that oceans had possibly formed by 4.2 Ga ago (VALLEY et al. 2006).

There is compelling evidence for marine life on Earth 3.5 Ga before present. This evidence stems from stromatolites (3.47 Ga; WESTALL et al. 2006) and carbon isotope fractionation (~3.52 Ga; BUICK 2007). The stromatolites are layered sedimentary structures resulting from the activity of probably phototropic microbes. The difference in ^{13}C depletion between carbonate and kerogens of some Early Archean rocks is consistent with the existence of photoautotrophic organisms. Similar carbon isotope signatures have been reported for even older rocks from the Hadean–Archean boundary and have been interpreted as evidence for life around 3.8 Ga (MOJZSIS et al. 1996; ROSING 1999). In these cases, however, the biological origin seems to be less certain (FEDO & WHITEHOUSE 2002; BUICK 2007). The interpretation of filamentous structures in ~3.465 Ga old rocks as microfossils is not generally accepted (SCHOPF 1993; BRASIER et al. 2002). Taken together, one can conclude that the transition from chemical to biological evolution had occurred by 3.5 Ga before present. Thus, the conditions on Earth and Mars in the period between 4.4 and 3.5 Ga formed the setting for the relevant prebiotic chemistry.

3.8 Ga ago, i. e. in the Late Hadean–Early Archean (corresponding to the Late Noachian eon of Mars, JAKOSKY & PHILLIPS 2001), Earth already looked much more similar to present-day Earth than to any other present-day planet. The surface was covered by an ocean from which active volcanic islands and possibly small short-lived protocontinents protruded (RUSSELL & ARNDT 2005; MARTIN et al. 2006). The salt content of the ocean was higher than today (KNAUTH 1998, 2005). Geological samples in which the composition of the ancient sea salt is preserved are unknown, but it seems safe to assume that, like today, chloride was the main anion and sodium, potassium, magnesium and probably calcium were the main cations. Due to the anoxic conditions (see below) the sulfate concentration was low, perhaps less than 1% of the modern value (HOLLAND 2004). The ocean was probably slightly acidic to neutral. MORSE & MACKENZIE (1998) calculated ~pH 5.8 for the Early Hadean and ~pH 6.8 for the Late Hadean seawater. As a consequence of the non-oxidizing and acidic environment, some transition metals existed in low oxidation states and were dissolved in the ocean in higher concentrations than today. Fe^{2+} is the most prominent example.

Our picture of the Late Hadean–Early Archean atmosphere has drastically changed with time. Originally

it was assumed that the primordial atmosphere contained high concentrations of hydrogen, methane and ammonia, and thus was similar to the present-day atmospheres of the giant planets Jupiter and Saturn. This idea was the basis for MILLER's famous simulation experiments, in which he demonstrated that amino acids easily form by electrical discharges in this kind of atmospheres (MILLER 1953, 1955). However, today a different model of the atmosphere before the emergence of life is favoured (KASTING & CATLING 2003; KASTING & HOWARD 2006; CATLING & KASTING 2007; SHAW 2008). Approximately 4 Ga ago, the main atmospheric constituents probably were nitrogen, carbon dioxide and water vapour. Model calculations indicate a partial pressure of free oxygen of $\sim 10^{-13}$ bar, in other words O_2 was practically absent near the surface (KASTING 1993)! As a consequence, a UV-absorbing ozone (O_3) layer was also missing. Therefore short wavelength UV radiation may have reached the planet's surface as it is the case on Mars today. It could have damaged organic molecules and thus affected the chemical evolution. However, other absorbers and scatterers of UV radiation that could have effectively protected the surface are conceivable. Among them are carbon dioxide, volcanic sulfur dioxide, a thin haze of organics produced by photoreactions of methane, and dust from volcanic eruptions and episodic meteorite impacts (WESTALL et al. 2006). Our present picture of the early atmosphere also assumes that the concentrations of hydrogen and ammonia were low because the former rapidly escaped into space and the latter was destroyed by UV radiation. The H_2 concentration was probably around 0.1%, although much higher values cannot be excluded (TIAN et al. 2005; KASTING & HOWARD 2006). Approximately 0.3 bar of the greenhouse gas carbon dioxide could have prevented the ocean from freezing (KASTING & CATLING 2003). Why was the early Earth in danger of glaciation? The answer lies in the solar luminosity which steadily increases with time. Around 4 Ga ago, the Sun was 20–30% less luminous than today. Therefore, without a sufficiently strong greenhouse effect, the mean surface temperature would have been below the freezing point of water ("faint young Sun problem"; KASTING & CATLING 2003). If the abiotic production rate of methane, which also acts as a greenhouse gas, was high enough, the CO_2 concentration could have been below 0.3 bar. HAQQ-MISRA et al. (2008) have calculated the effect of (biogenic!) methane and organic haze on the temperature 2.8–2.2 Ga ago when the Sun's luminosity was ~20% lower than today. They found that 0.03 bar of CO_2 and 3000 ppm of CH_4 could have kept the mean surface temperature at $\sim 17^\circ C$. It is unknown how far above the freezing point the early Earth's temperature was, but there are some indications of a moderate climate with temperatures well below $70^\circ C$ (KASTING & HOWARD 2006; KASTING & ONO 2006). While the bulk atmosphere was probably mildly reducing, volcanic exhalations could

have locally created more strongly reducing conditions which facilitated the abiotic synthesis of organic compounds. Volcanic islands as special locations of chemical evolution will be discussed in the next chapter.

Another difference between the Earth in the Hadean eon and today is the frequency of meteoroid, asteroid and comet impacts. A much higher flux of impacting objects prior to 3.8 Ga before present is documented in the geological record of the Moon. Some of the impactors that hit the Earth might have had diameters of a few hundred kilometres (SLEEP et al. 1989). For comparison, the Chicxulub impactor which triggered the mass extinction at the Cretaceous–Paleogene boundary ~65.5 million years ago had a diameter of only ~10 km. There is a spike in the impact rate curve at ~3.9 Ga known as the Late Heavy Bombardment (LHB). The LHB has been explained by a rapid migration of the giant planets that caused perturbations in the inner solar system (“Nice model”; GOMES et al. 2005). SLEEP et al. (1989) have argued that due to the environmental effects of large impacts certain ecosystem could not have continuously existed on Earth before the end of the LHB. Other authors have concluded that these effects were less dramatic, for example that no global sterilization could have occurred during the LHB (ABRAMOV & MOJZIS 2009). Possibly “the Earth from ~4.4 Ga to ~3.8 Ga was comparatively peaceful” (RYDER 2003). Instead of delaying the emergence of life, impactors probably accelerated the chemical evolution. Some of them delivered organic compounds to the Earth (“lithopanspermia” in the broadest sense). For example, a diverse inventory of abiotically formed organics has been found in carbonaceous chondrites, a certain class of stony meteorites (BOTTA & BADA 2002; SEPHTON 2002). Impacts also produced organic molecules, either directly by shock synthesis (CHYBA & SAGAN 1992) or by increasing the CO-to-CO₂ ratio of the atmosphere (KASTING 1990). Compared to CO₂, CO gives higher yields of (at least some) organic compounds in simulation experiments, though it is less effective than CH₄. This has been demonstrated, for example, for the formation of the amino acid glycine (SCHLESINGER & MILLER 1983).

Today our neighbour planet Mars is a cold world with no persistent liquid water and only a thin atmosphere. This has been different in the Noachian eon (4.6–3.7 Ga before present). Though there are still many open questions about the conditions on the early Mars (KERR 2008), the following scenario seems probable (JAKOSKY & PHILLIPS 2001). In the Noachian, liquid water flowed at the Martian surface. This can be inferred from geological features that are difficult to explain by other causes (BAKER 2001). Lakes of salty water may have existed. The discovery of chloride-containing surface deposits supports this possibility (OSTERLOO et al. 2008). A wet Noachian Mars is also consistent with the presence of ancient clay minerals that must have been formed by aqueous weathering (CHEVRIER

& MATHÉ 2007; WRAY et al. 2009). It is interesting to note that clays may have played a key role in prebiotic chemistry, for example as catalysts (BRACK 2006). As in the case of the Hadean Earth (see above), greenhouse warming was necessary to sustain liquid water on Mars. Probably the ancient atmosphere mainly consisted of CO₂, but its density appears to have been limited by the UV instability of this gas (ZAHNLE et al. 2008). There are strong indications for Noachian volcanism, for example in the Tharsis region of Mars (NIMMO & TANAKA 2005). Therefore volcanic gases such as H₂S and SO₂ might have sufficiently enhanced the greenhouse effect of a relatively thin CO₂ atmosphere (JOHNSON et al. 2008b). Moreover, the transformation of SO₂ into sulfuric acid might have inhibited carbonate formation and thus allowed a thicker CO₂ atmosphere (BULLOCK & MOORE 2007). Model calculations have shown that CO was photochemically formed from CO₂ (ZAHNLE et al. 2008). As discussed above, atmospheric CO was probably beneficial to chemical evolution. Impactors also hit the early Martian surface – with all the consequences for prebiotic chemistry. On the whole we can say that on the Noachian Mars and the Hadean Earth the conditions for chemical evolution were probably not very different.

3. Planetary chemical evolution and its laboratory simulation

The term “evolution” is frequently identified with biological evolution. However, evolution is a much more universal concept which, in principle, can be applied to any more or less continuous development that produces ever-increasing complexity. Open-endedness may be added as a further criterion. For example, human language (CORBALLIS 2009) and the mineral world (HAZEN et al. 2008) are characterized by evolution. Chemical evolution, which started with the formation of the first elements (nucleosynthesis, see above and Fig. 1), comprises prebiotic chemistry, i. e. those chemical processes from which the first organisms resulted. Though the exogenous delivery of organic compounds (CHYBA & SAGAN 1992) demonstrates that prebiotic chemical evolution has a non-planetary component, the chemistry that was more close to the origin of life must have proceeded on Earth or Mars. Therefore the following discussion will focus on planetary aspects of chemical evolution.

Several experimental and theoretical approaches have been developed to solve the riddle of the origin of life, but up to now there has been no breakthrough. In the following I will discuss some more general aspects instead of giving a survey of individual hypotheses. Detailed descriptions of most of these hypotheses can be found in BRACK (1998), GARGAUD et al. (2005) and SULLIVAN & BAROSS (2007).

Today it is generally accepted that life did not come into existence by a sudden event but as DE DUVE (1991: 112) has put it: "... it may be taken as virtually certain, unless one adopts a creationist view, that life arose through the succession of an enormous number of small steps, almost each of which, given the conditions at the time, had a very high probability of happening". So the problem is to find out which steps might have occurred in which order. There are two alternative ways to tackle this problem, namely "top-down" and "bottom-up". The top-down approach is a back-extrapolation that starts from chemical features of extant cells and progressively simplifies them. Therefore it is often preferred by molecular biologists and biochemists. In principle it is a powerful tool which leads us back in time and may provide clues to the ancient biochemistry, perhaps even before the last universal common ancestor (WHITFIELD 2004) existed. However, the top-down approach becomes unreliable before the transition from chemical to biological evolution because the chemistry of prebiotic systems may have left no traces in modern biochemistry. CAIRNS-SMITH (1982: 95–99) gave the following analogy. A complex structure of arches of stones (representing modern biochemistry) can only be constructed by adding and removing scaffolds (representing no longer existing prebiotic or early biotic chemistry). It is nearly impossible to recognize from the final arch structure which scaffolds existed during its "evolution". The bottom-up approach may be regarded as more promising especially if one follows DE DUVE (1991) in assuming that chemical evolution proceeded in highly probable steps. This approach starts from a basic inventory of compounds that were very probably present on the early Earth and Mars. It then tries to simulate the succeeding chemical steps that produced increasingly complex systems. There are two main prerequisites for this approach to be successful. First, the primordial environmental conditions must be known in order to be able to simulate them. As described in the preceding chapter, we have a rough picture of the early Earth's and Mars' environments though several uncertainties and open questions remain. Secondly, we should not be guided by the way chemists usually think about laboratory synthesis. Instead of optimizing reaction conditions in order to obtain a target molecule in high yield, we should properly simulate likely prebiotic conditions and simply learn from the experimental results. This latter point has been stressed by SHAPIRO (2007, 2008).

RNA is both an information carrier and a catalyst. Therefore it is not unrealistic to assume that an "RNA world" existed in which advanced protocells were based on RNA instead of DNA and proteins (GESTELAND et al. 2006). However, the idea of an RNA world very early in chemical evolution is much less convincing because the de novo appearance of RNA in the "primordial soup" seems virtually impossible. Current knowledge tells us that the

sheer complexity of RNA polymers would have precluded their spontaneous formation (SHAPIRO 2006, 2007):

(i) Abiotically formed nucleobases and D-ribose must have been available in sufficient concentrations and purities. They had to combine to nucleosides without the formation of products that could have interfered with the subsequent reactions. Then the nucleosides and phosphate must have formed nucleotides. An alternative route to pyrimidine nucleotides uses cyanamide, glycolaldehyde, glyceraldehyde, cyanoacetylene, phosphate, and urea (POWNER et al. 2009). Here the right sequence of reactions, the availability of the starting materials and the high concentrations used in some steps make heavy demands on the prebiotic conditions.

(ii) The condensation of nucleotides is thermodynamically unfavourable and therefore proceeds only after chemical activation. However, the prebiotic existence of activating agents has not yet been convincingly demonstrated.

(iii) Even if activated nucleotides existed, several other prebiotic compounds would have reacted with them. For example, the termination of growing RNA chains by monofunctional molecules must have been a severe problem.

Other replicators have been suggested as precursors of RNA ("pre-RNA world", SHAPIRO 2007). Among them are peptide nucleic acids (PNA). The backbone of PNA is built from diamino monocarboxylic acids that have been found in very low concentrations in the Murchison meteorite (see STRASDEIT (2005) for an overview). PNA avoid some problems that occur with RNA (e. g. homochirality, prebiotic sugar syntheses) but several others continue to exist (e. g. concentration of monomers, chemical activation, chain termination). The spontaneous formation of prebiotic functional polymers is very improbable. This is not only true for possible genetic materials but also for polypeptides. In the case of short oligopeptides the situation appears to be different. The environmental conditions on early Earth and Mars very probably allowed the spontaneous condensation of a limited number of amino acid molecules. RODE (1999) and coworkers obtained mainly dipeptides by heating α -amino acids in concentrated Cu(II)-containing NaCl solutions. The conditions of this salt-induced peptide formation (SIPF) reaction simulate the evaporation of seawater at a primordial hot volcanic coast. When glycine in clay minerals is kept at 200 °C, oligomers up to the hexapeptide are formed within two days (DALAI & STRASDEIT 2010). These experiments, too, are realistic simulations of prebiotic conditions because it is practically certain that clays were present in large amounts on early volcanic islands. Despite several different experimental attempts no long-chain peptides have been obtained from non-activated amino acids under simulated prebiotic conditions. Thus the existence of an early "protein world" also appears improbable. If polymers were not initially available, then what was the chemistry of the

first ordered systems that emerged in planetary chemical evolution? A possible answer could be a “metabolism” that started from small molecules.

It is conceivable that life began as assemblies of monomers and short oligomers. These molecules were involved in nets of coupled reactions and formed what has been called mutually catalytic or collectively autocatalytic sets (DYSON 1999; SEGRÉ et al. 2000; SEGRÉ & LANCET 2000; SHAPIRO 2006; KAUFFMAN 2007). The passage from a chaotic primordial soup to such ordered sets can be described as a phase transition and is thus distantly related to crystallization (KAUFFMAN 1993). The evolution and general properties of an early metabolizing system are depicted in Fig. 2. The hypothetical scenario consists of four stages A–D:

A. Diverse abiotically formed small molecules were present on the Hadean–Early Archean Earth and probably also on the Noachian Mars. They ranged in size from di- and triatomic (e.g. CO, HCN) to a few dozen atoms (e.g. short peptides). These molecules had been synthesized on the planets or delivered by impactors (CHYBA & SAGAN 1992), as briefly discussed above. No functional polymers existed but polymeric materials such as the insoluble organic matter of carbonaceous chondrites, minerals, and possibly thermal products related to graphite and charcoal were present. As the distribution of the small molecules was far from equilibrium, their concentrations and mixing ratios strongly varied with the location. Hun-

dreds or even thousands of these compounds must have existed, among them inorganic salts, carboxylic acids, amino acids, short peptides, sugars, and (hetero)aromatic compounds. The fact that in the Murchison meteorite alone more than 70 amino acids have been identified gives an impression of the prebiotic chemical diversity (BOTTA & BADA 2002).

B. The next step was the selection of certain molecules from the primordial soup. In Fig. 2, a membrane allows only those molecules that possess the property “green” to enter a compartment. This compartment could be a vesicle that has a bilayer membrane composed of amphiphiles (POHORILLE & DEAMER 2009). Amphiphiles are molecules that contain a polar and a non-polar group. It is well known that under suitable conditions such molecules self-assemble to form vesicles. This is a first important step in the transition from chaos to order. Fatty acids and their esters are examples of amphiphilic molecules that might have been present on the early Earth and Mars. It is plausible that the first membranes exhibited only rudimentary selectivity. In the model shown in Fig. 2 the membrane selects by colour but cannot distinguish between the molecular shapes (circle, square, triangle). The building blocks of membranes are not constrained to fatty acids and their derivatives. For example, colloidal iron(II) sulphide (FeS) has been suggested as an alternative (RUSSELL & HALL 1997). In principle, a compartment can also be two-dimensional, i.e. a surface. This idea was especial-

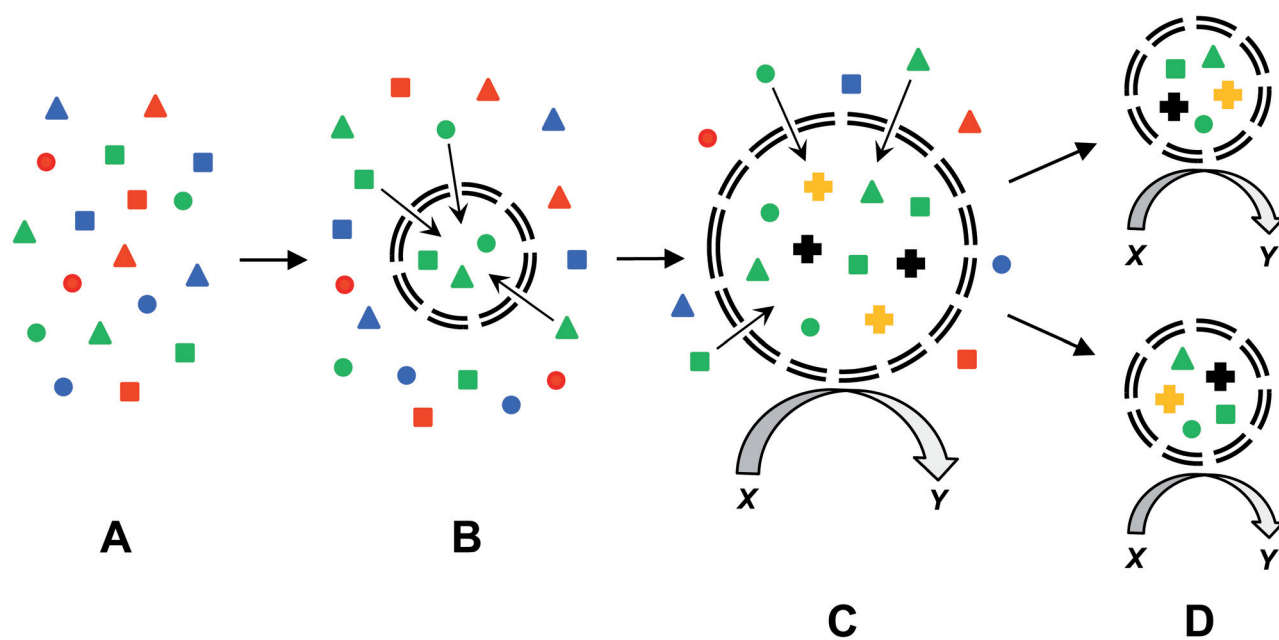


Fig. 2. Schematic representation of the possible origin and properties of the first metabolizing systems. The stages A–D are explained in the text. The coloured objects symbolize different molecules.

ly developed by WÄCHTERSCHÄUSER (1988) who proposed the evolution of a metabolism on mineral surfaces. Minerals can also enhance the formation of fatty acid-based vesicles (HANCZYC et al. 2007).

C. In the next step the phase transition took place. The “green” molecules of Fig. 2 established an autocatalytic reaction net and produced new molecules (the black and yellow crosses in Fig. 2). Thus the “green” molecules served as nutrients. Laboratory experiments have shown that vesicles composed of simple amphiphiles have a relatively high permeability (DEAMER 2008; MANSY et al. 2008). If small metabolites were autotrophically synthesized, e.g. from carbon dioxide, they would have leaked out. It was therefore concluded that the first protocells were probably heterotrophs. Although most metabolism-first hypotheses assume an autotrophic origin, metabolism-first does not exclude heterotrophy. The organic nutrients that entered the compartment could have been transformed into oligomers and polymers. These products were unable to permeate the membrane. In fact, the interplay between the composition of the membrane, which determined the permeability, and the nature of the products could have been part of the evolutionary process. The autocatalytic reaction net needed energy to function and therefore must have been coupled to an external energy supplying system. The transition of this system from a state of high to a state of low free energy ($X \rightarrow Y$) has been called the “driver” reaction (SHAPIRO 2006). The prebiotic environment offered different forms of energy, for example heat, sunlight and chemical energy (in bonds, redox systems, pH gradients) (DEAMER & WEBER 2010).

D. When a compartment divided, the reaction net was transmitted to both daughter protocells. Thus, inheritance was made possible by the existence of a “compositional genome” (SEGRÉ et al. 2000; SEGRÉ & LANCET 2000). If this model is right, identical reproduction can occur independent of replication, although with a higher error rate. Different compartments developed different chemical inventories. Some of them became the cradle of replicators and protoenzymes.

Before producing functional polymers, the protocells must have synthesized a pool of homochiral compounds. A discussion of the diverse aspects of the origin of bio-homochirality is beyond the scope of this paper (for a review on this topic, see: CRONIN & REISSE 2005). However, it shall be mentioned that it has recently been suggested to regard the origin of homochirality and the origin of life as the same event (CARROLL 2009). In other words, life has been defined via homochirality. Should the self-sustaining and self-reproducing chemical systems of the type described above considered alive? The answer, of course, depends on how we define life. As the transition between non-living and living matter is gradual, every fixation of a sharp boundary must be artificial. Consequently, there

is no consensus definition of life (LAHAV 1999; CLELAND & CHYBA 2007). It has even been questioned whether this issue is of major interest at all (BRUYLANTS et al. 2010). Nevertheless, in some areas such as the search for extra-terrestrial life it may be necessary to have an operational definition of life.

Going back to step B of Fig. 2, one might ask in which locations which molecules were available with a high probability. The following example shows how this problem can be tackled by accurate simulation of prebiotic conditions. There are good reasons to believe that volcanic islands were important places for chemical evolution. For example, volcanic lightning in ash–gas eruption clouds very probably produced amino acids (JOHNSON et al. 2008a). These compounds, which also came from other abiotic sources such as meteorites, dissolved in the seawater. When lava flowed into the ocean, the seawater evaporated. Subsequently, the remaining sea salt crusts experienced temperatures up to some hundred degrees on the hot basalt. The formation and heating of salt crusts can still be observed today. 4 Ga ago, the abiotically synthesized amino acids were embedded in the solid sea salt. We have called this the “hot-volcanic-coast scenario” (STRASDEIT & FOX 2008). It has been simulated by studying the thermolysis of glycine, DL-alanine, α -aminoisobutyric acid and some other α -amino acids under different conditions. Most neat amino acids sublimed on heating, with the remarkable exception of glycine which decomposed to form an insoluble residue. Sublimation also occurred when the solid mixtures that were obtained by evaporation of NaCl–KCl–amino acid solutions were heated. However, when $MgCl_2$ and $CaCl_2$ were additionally present, the thermolyses yielded alkylpyrroles among other organic products. Thus, the composition of the artificial sea salt turned out to be crucial. The reason lies in the formation of magnesium and calcium amino acid complexes which prevent the amino acids from subliming. These results demonstrate how small changes of environmental conditions can drastically change chemical behaviour (YUSENKO et al. 2008; FOX & STRASDEIT 2009). If heterotrophic protocells existed at primordial volcanic coasts, they may have incorporated the abiotically formed alkylpyrroles and transformed them into oligopyrroles. The latter may have served as the first photoreceptors and electron-transfer molecules in a primitive metabolism.

Finally, a note of caution is necessary because at present, central features of the metabolism-first idea depicted in Fig. 2 are purely hypothetical. In fact, the theoretical models on which metabolism-first hypotheses are based have been criticized (ANET 2004). From the analysis of one of these models it has been concluded that compositional genomes lack evolvability (VASAS et al. 2010). However, we must keep in mind that a mathematical model may or may not appropriately describe a real chemical

system. Therefore, both the idea of a metabolism-first and a replication-first origin of life remain appealing, but at the same time there are doubts about the chemical feasibility under prebiotic conditions. Results of future experiments will show which ideas have to be abandoned: “The great tragedy of science – the slaying of a beautiful hypothesis by an ugly fact” (HUXLEY 1870).

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